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Surface current reduction of (211) oriented $Cd_{0.46}Zn_{0.04}Te_{.50}$ crystals by Ar bombardment

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Abstract

$Cd_{0.46}Zn_{0.04}Te_{.50}$ crystals have been exposed to high density Ar plasmas in order to modify the surface chemistry and control the surface conductivity. X-ray photoelectron spectroscopy (XPS) reveals that this bombardment results in a modified surface atomic ratio, with Cd being preferentially removed compared to Te. In addition, the native oxide is removed and suppressed for an extended period of time. Current-voltage data is analyzed in order to determine the effect on surface leakage current after exposure. It is found that surface leakage current can be decreased by approximately 2.5 orders of magnitude following Ar^{+} bombardment.

I. INTRODUCTION

CdZnTe is a material of significant interest for both room temperature x-ray and gamma ray detection. [1, 2] It exhibits none of the polarization phenomenon that can degrade the performance of CdTe detectors [3, 4] while at the same time allowing for excellent energy resolution with specialized single polarity charge sensing electronics. Improvements in the crystal growth have yielded CdZnTe crystals with decreased bulk defects and precipitates, which can act as traps and degrade detector performance. However, crystal sizes are still small, properties non-uniform, and much work remains to be done. [5] In addition, the use of pixellated [6] or coplanar grid electrodes [5] combined with advanced signal processing has advanced the state of the art towards near the Fano limit for this type of detector.

To achieve further improvements, understanding and control of the surface chemistry and electronic properties is necessary. Reductions in the surface leakage current can help to achieve superior energy resolutions for the varying types of detector structures commonly used in CdZnTe gamma detectors. Numerous dry and wet chemical surface preparations and metals have previously been explored, both for improved electrical contact properties and reduced surface leakage current. [7-10] However, CdZnTe surfaces seem to be poorly understood and still suffer from issues with inconsistency and reproducibility. It is generally believed that this is due to bulk inhomogeneities within the crystal [11]. In addition, the presence of surface states that result from unsatisfied bonds and the termination of crystalline symmetry at a material surface can result in both surface leakage current and Fermi pinning. Finally, because of its crystal structure, the faces of CdZnTe are polar and are terminated with either Cd or Te (A or B face). This can control the electrical behavior of deposited contacts as well as the surface leakage current. Common themes in surface treatments include the removal of native oxide and restoration of a more desired oxide as well as affecting changes in the surface atomic ratio. A significant amount of work has been done on CdZnTe surface preparation for growth of HgCdTe infrared

detectors, with the usual goal being the removal of C and O surface contamination and a stoichiometric surface. [12]

In this work, we describe the effect of energetic Ar ion bombardment from high-density plasmas on the surface composition and surface leakage current of (211)-oriented $Cd_{0.46}Zn_{0.04}Te_{.50}$. It is found that Ar ion bombardment preferentially removes Cd as compared to Te, as predicted by Stopping Range of Ions in Matter (SRIM 2008) calculations. Bombardment can achieve the removal of the native surface oxide as well as modifying the atomic ratio at the surface, which in turn affects the composition of a new native oxide. The effect on surface conductivity of these treatments is examined, with effects resulting from removal and regrowth of native oxide, changes in surface atomic ratio, and ion induced damage considered. We observe a large decrease on the order of 2.5 orders of magnitude in the surface leakage current on the A surface.

II. EXPERIMENT AND RESULTS

A. Experimental details

High resistivity (211)-oriented $Cd_{0.96}Zn_{0.04}Te$ crystals patterned with Pt electrodes were subjected to energetic ion bombardment in high density plasmas. The A (nominally Cd rich) and B (nominally Te rich) crystal faces were exposed in a Perkin-Elmer sputter chamber to a high density Ar plasma operating at 6 mTorr, 135 sccm Ar, 750W, and 400V DC Bias for 1 minute each. X-ray photoelectron spectroscopy (XPS) was used to determine the effect of plasma exposure on surface composition. Current-voltage (IV) measurements were used to determine the surface electrical characteristics and effect of the different ion bombardment conditions.

XPS analysis was performed on a PHI Quantum 2000 system using a focused monochromatic Al Kα X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. A 200 μm diameter X-ray beam was used for analysis. The X-ray

beam is incident normal to the sample and the X-ray detector is at 45° away from the normal. The pass

energy was 23.5 eV giving an energy resolution of 0.3 eV that when combined with the 0.85 eV full

width at half maximum (FWHM) Al Kα line width gives a resolvable XPS peak width of 1.2 eV FWHM.

Deconvolution of non-resolved peaks was accomplished using Multipak 6.1A (PHI) curve fitting routines.

The collected data were referenced to an energy scale with binding energies for Cu $2p_{3/2}$ at

932.72 ± 0.05 eV and Au $4f_{7/2}$ at 84.01 ± 0.05 eV. Binding energies were also referenced to the C 1s

photoelectron line arising from adventitious carbon at 284.8 eV. Low energy electrons and Ar^+ ions were

used for specimen neutralization.

B. Effect of energetic Ar^+ ion bombardment on surface composition

The effect of energetic Ar^+ ion bombardment on the surface composition has been examined

through the use of XPS measurements. As received CdZnTe (211)-oriented A and B surfaces were

examined using XPS. Atomic concentration ratios were determined by comparing the peak area ratios

of the Cd $3d_{3/2}$ core level at ~405 eV and the Te $3d_{5/2}$ level at ~573 eV. Measuring the existence of CdO is

not possible due to resolution limits of the system (~0.8 eV), but can be inferred from the full width half

maximum (FWHM) of the Cd peak. The TeO_2 peak is located at ~576 eV and is clearly visible when

present. The Zn $2p_{3/2}$ peak at ~1021 eV was included in the measurements, as well. In addition, peaks

for O and C were obtained. The surfaces were measured in the XPS, then exposed to the Ar plasma in

the sputter chamber for 1 minute before being remeasured in the XPS.

Table 1 presents the Cd:Te and Cd:Zn peak area ratios for the as received and Ar ion treated

surfaces. These results confirm that the as received CdZnTe(211)A face is Cd rich. Figures 1 and 2 show

the Te $3d_{5/2,3/2}$ spin-orbit pair for the plasma exposure and for the LDP exposure, respectively. The lower

energy peak at ~573 eV represents Te bound to Cd, while that at ~576 eV is assigned to TeO_2. These

spectra clearly demonstrate that the as received surfaces are Cd rich, and that the Cd:Te ratio can be

reduced with exposure to an Ar plasma. In addition, although the XPS system is not located in-situ with

the sputter chamber, it is clear that the surface oxide is removed by the plasma treatment from the reduced height of the TeO_2 peak as compared to that of Te. Some amount of reoxidation occurs during specimen transfer. The removal of Cd preferentially to Te by Ar bombardment is expected and predicted from SRIM 2008 simulations. Figure 2 shows the simulated ion sputter yield of Cd, Zn, and Te atoms vs incident ion energy for a film with the same bulk composition of our samples. Clearly, Cd will be removed prefentially.

C. Effect of energetic Ar^+ ion bombardment on electrical characteristics

In order to determine the effect of plasma exposure on the electrical properties of the surface, Pt contacts of varying diameters were deposited on both A and B surfaces of untreated CZT crystals. Current-voltage measurements were taken prior to plasma exposure, immediately following plasma exposure, and repeated over the course of two weeks. Characteristic IV curves for both A and B surfaces are shown in Figures 3 and 4 for 500 um diameter devices.

From these, it is clear that plasma exposure leads to a significant change in the electrical properties of the surface. On the A side, the current is greatly suppressed immediately following exposure with a further decrease occurring as the oxide regrows, with a total change of more than 2.5 orders of magnitude. This is likely due to the significant change in the Cd:Te ratio and a modified native oxide composition. For the B side, an initial increase in the current following oxide removal is noted immediately following plasma exposure. Regrowth of the oxide results in a decrease in the surface, resulting in similar characteristics to the pristine surface. Note that the IV curves of the A surface after plasma exposure and oxide regrowth possess similar magnitudes of current to the B surface, which is consistent with prior observations from XPS analysis as well as SEM images.

The bulk and surface components of leakage current can be separated by analyzing the reverse current density (J_r) versus the peripheral to area ratio of different size electrodes, with the equation

$J_r = J_{rv} + J_{rp}(P/A)$, where J_{rv} is the bulk component, J_{rp} is the periphery component, and P/A is the periphery:area ratio. The surface leakage component is then described by the relation $J_{rs} = J_{rp}(P/A)$. We monitored the change in J_{rp} as a function of time. Figure 5 displays this for the A and B sides at 10V.

Figure 5 clearly shows a large decrease in surface leakage for the A face immediately following plasma exposure, with further decrease over time as the oxide regrows, indicating the change observed in Figure 3 directly results from the modification of the surface.   For the B face, it shows a large increase, followed by a similar decrease as the oxide regrows. At 10V, the plasma exposed B surface recovers to nearly the same J_{rp} value as the unexposed surface. The slight increase is likely due to plasma induced defect states at the surface, which could slightly enhance conduction.

Conclusions

Energetic Ar$^+$ ion bombardment of CdZnTe surfaces has a drastic effect on the electrical properties. The primary effect appears to be the modification of the Cd:Te ratio. This value differs depending on the face of the crystal examined. Modification of this ratio results in significant changes in the surface conductivity, as the composition and thus conductivity of the regrown native oxide is changed. Specifically, following plasma exposure the surface leakage current on the A face is decreased by approximately 2.5 orders of magnitude. This suggests that an optimal surface treatment regimen will consider the composition of the native oxide produced, and will modify the Cd:Te ratio at the surface to achieve it. Further, the strong dependence of the surface electrical characteristics on this ratio suggests that development of contacts to CdZnTe can be improved by controlling this ratio. Future work will focus on controlling the interface at the contacts in order to understand the mechanisms which control their characteristics and then to minimize injected leakage current.

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List of Tables

Table 1

	Cd:Te	Cd:Zn
A-face as received	1.61	-
B-face as received	1.21	-
A-face 1 min plasma	1.14	-
B-face 1 min plasma	1.01	-

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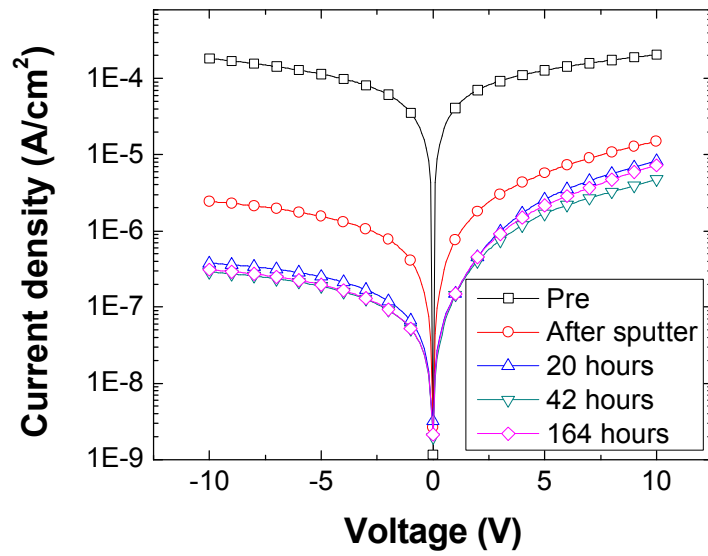**List of Figures**

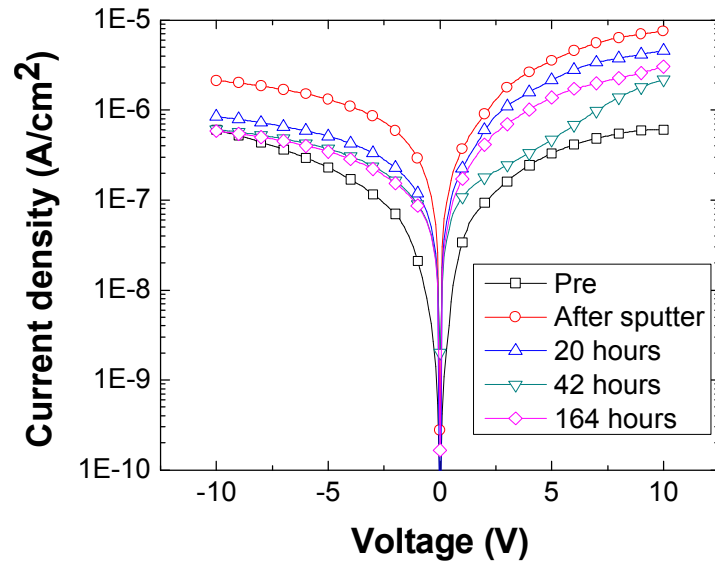**Figure 1**

Te 3d$_{5/2}$
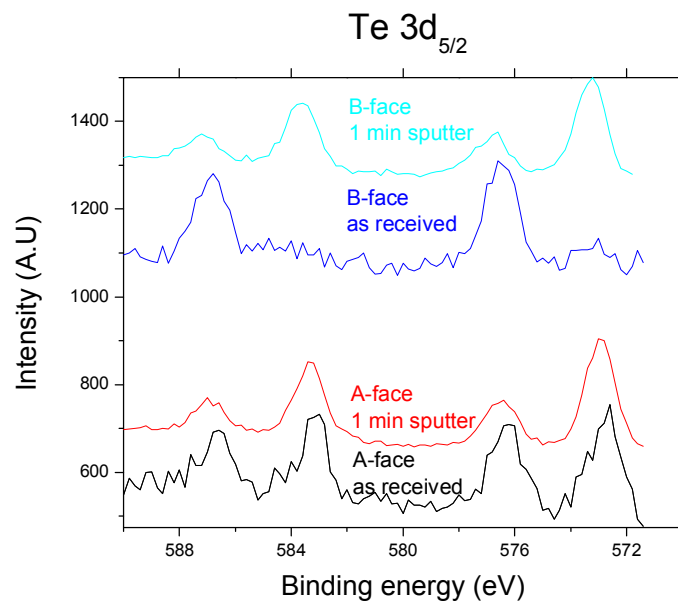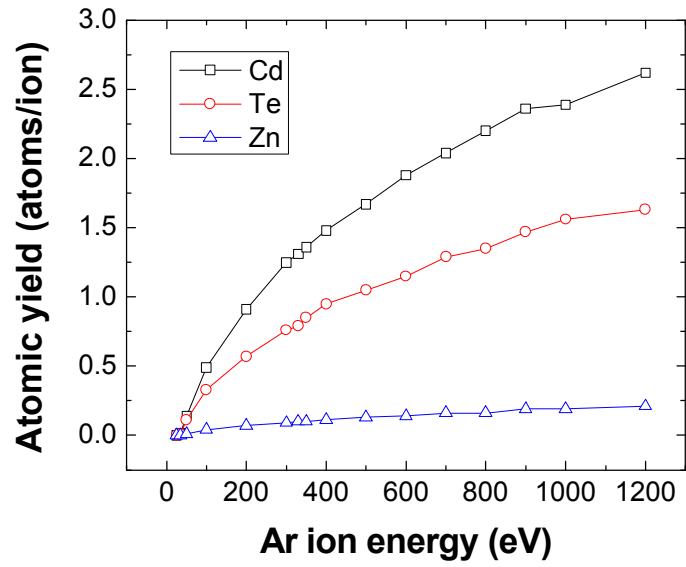
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Figure 2

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Figure 3

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Figure 4

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Figure 5

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